Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Photoresponsiveness of Anthracene-Based Supramolecular Polymers Regulated via a σ -Platinated 4,4-Difluoro-4-bora-3a,4adiaza-s-indacene Photosensitizer

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Supporting Information

ABSTRACT: Anthracene and its derivatives have attracted tremendous interest in recent years because of their intriguing photoresponsive behaviors. Our research group has previously constructed anthracene-based supramolecular polymers, which display multicycle anthracene-endoperoxide photoswitching in a macroscopic manner. However, high-energy light excitation ($\lambda = 365-460$ nm) is required for anthraceneto-endoperoxide photooxygenation, giving rise to severe photodegradation problems. In this work, we have developed an effective approach to addressing this issue, by encapsulating a σ -platinated 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) photosensitizer into anthracene-based supra-



molecular polymeric systems. The platination effect enhances π -electron delocalization, while promoting intersystem crossing from singlet to triplet excited states. Accordingly, the σ -platinated BODIPY photosensitizer displays excellent ${}^{1}O_{2}$ production capability, facilitating anthracene-to-endoperoxide transformation under low-energy irradiation conditions ($\lambda = 520-590$ nm). This leads to the breakup of supramolecular polymers and gels, which can be restored at room and elevated temperatures because of the reversible endoperoxide-to-anthracene deoxygenation process. Overall, the rational design of a σ -metalated photosensitizer opens up a new avenue to regulating the photoresponsiveness of supramolecular polymers under mild and nondestructive conditions.

1. INTRODUCTION

Supramolecular polymers, representing the polymeric arrays of monomeric units held together by directional and reversible noncovalent bonds,¹ are endowed with fascinating adaptive and self-healing properties.² Light is one of the attractive external stimuli in terms of its remote and clean character, which stimulates the incorporation of photoresponsive building blocks into supramolecular polymers.³ In this respect, anthracene and its monosubstituted derivatives represent intriguing candidates capable of undergoing the well-known [4 + 4] and/or [4 + 2] photodimerization reactions.⁴ For 9,10disubstituted anthracenes, anthracene-to-endoperoxide photoswitching takes place upon light irradiation.⁵ Our research group has previously constructed one-dimensional supramolecular polymers on the basis of 9,10-disubstituted anthracene monomer 1 (Scheme 1).5c The supramolecular polymerization process is synergistically driven by multiple hydrogen-bonding and π - π -stacking interactions because of the presence of two amide units on 1.6 Photooxygenation of 1 to its endoperoxide form (1-O₂; Scheme 1) takes place upon light irradiation, while backward conversion occurs sponta-

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neously at room temperature. The quantitative anthraceneendoperoxide photoswitching leads to macroscopic photoresponsiveness of the supramolecular polymers (Scheme 1).

Despite the progress achieved so far, blue visible light (λ = ~460 nm) or long-wave UV light ($\lambda = ~365$ nm) is required for the anthracene-to-endoperoxide photooxygenation of 1 (Scheme 1).5c High-energy irradiation gives rise to an unavoidable photodegradation issue.⁷ In this regard, it is desirable to trigger photoresponsiveness under mild conditions. A plausible approach to attaining this objective is to encapsulate a photosensitizer into the supramolecular polymeric systems. Upon excitation of the photosensitizer via lowenergy visible light, reactive oxidized species can be generated in situ, which, consequently, react with 1 and facilitate the disassembly of supramolecular polymers.

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) represents a fascinating class of visible-light photosensitizers.⁸ The parent BODIPY chromophore displays intense absorbance in

Received: July 11, 2019

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Scheme 1. Schematic Representation for Regulating the Photoresponsiveness of a One-Dimensional Supramolecular Polymer Derived from 1 via the σ -Platinated BODIPY Photosensitizer 2



the green region ($\lambda = \sim 500$ nm; Scheme 2). To extend absorbance in the low-energy region, a feasible approach is to





incorporate π -conjugation units at the methyl or α position of the pyrrole moieties (Scheme 2).⁹ An alternative protocol involves the fusing of π -aromatic rings to the BODIPY chromophore (Scheme 2).¹⁰ Although metalation can also be regarded as a plausible way to modulate the absorbance of

BODIPY, this strategy has received much less attention compared to the aforementioned ones.¹¹

Herein, σ -platinated BODIPY 2 (Scheme 1) has been employed as an efficient photosensitizer to regulate the photoresponsiveness of one-dimensional supramolecular polymers derived from 1. The design principle is based on the following considerations. First, both 1 and 2 feature a similar platinum acetylide unit,¹² which facilitates the embedment of a photosensitizer into the rod segment of supramolecular polymers. Second, d-p orbital overlap takes place between platinum(II) and the 2,6-diacetylene BODIPY ligand on 2.13 The enhancement of π -electron delocalization results in a red shifting of the absorbance signal.¹³ Third, 2 tends to undergo intersystem crossing (ISC) upon light excitation, which provides ¹O₂ to the neighboring monomer 1.¹⁴ Accordingly, photooxygenation of 1 is operated via low-energy visible-light irradiation. This leads to the breakup of supramolecular polymers, which can be restored at room temperature because of spontaneous conversion from $1-O_2$ to 1 (Scheme 1). Hence, employment of a σ -platinated photosensitizer represents an effective approach to modulating the responsiveness of supramolecular systems under nondestructive photoirradiation conditions.

2. RESULTS AND DISCUSSION

Synthesis of σ -Platinated BODIPY 2. The synthetic route toward 2 is quite straightforward (Scheme 3). Briefly, the BODIPY skeleton 3 is obtained via condensation reaction between benzaldehyde and 2,4-dimethylpyrrole, which is further iodinated to provide the intermediate 4. 4 is reacted

Scheme 3. Synthetic Route toward the σ -Platinated BODIPY Photosensitizer 2^{*a*}



^{*a*}DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

with (trimethylsilyl)acetylene to form **5** via the Sonogashira reaction, followed by deprotection of the trimethylsilyl (TMS) unit. The final step involves a copper-catalyzed coupling reaction between the deprotected form of **5** and *trans*- $[PtI_2(PEt_3)_2]$. The chemical structure of **2** is verified by means of ¹H, ¹³C, and ³¹P NMR and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra (Figures S1–S4). The ³¹P NMR spectrum of **2** shows one signal at 9.00 ppm in chloroform-*d* (Figure S3). The equivalence of the phosphorus atoms validates the trans configuration of the triethylphosphine units.

Spectroscopy of σ **-Platinated BODIPY 2.** UV-vis spectroscopy measurement is then performed for **2**. In trichloromethane (CHCl₃), it possesses a broad intense band from 500 to 700 nm (abbreviated as band I, $\varepsilon = 5.96 \times 10^4$ dm³ mol⁻¹ cm⁻¹ for the maximum absorption at 632 nm), together with a relatively weak absorbance at 350–500 nm (abbreviated as band II, $\varepsilon = 1.89 \times 10^4$ dm³ mol⁻¹ cm⁻¹ at 417 nm; Figure 1a). Both bands are bathochromic-shifted from



Figure 1. (a) UV–vis and (b) emission spectra of 2 (red lines) and 5 (black lines) in CHCl₃ ($c = 1 \times 10^{-5}$ M for each compound).

those of TMS-substituted BODIPY **5** ($\lambda_{max} = 557$ nm for band I, and $\lambda_{max} = 394$ nm for band II). Meanwhile, **2** also displays a more red-shifted emission signal than that of **5** ($\lambda_{max} = 670$ and 575 nm in CHCl₃, respectively; Figure 1b). The relative quantum yield (Φ_F) of **2** is determined to be 0.033, which is significantly lower than that of **3** ($\Phi_F = 0.527$). The result suggests emission quenching upon σ -plantination of BODIPY. The emission lifetime is determined to be 5.75 ns for **5** in chloroform (Figure S5a), validating the fluorescent emission lifetime is

0.39 ns for the aerated sample (Figure S5b). For the deaerated sample, a longer emission lifetime of 32.9 μ s is detected (Figure S5d), supporting the presence of phosphorescent emission. Accordingly, ISC takes place for 2 from singlet to triplet excited states, leading to dual-emission character.

We then resort to density functional theory (DFT) and time-dependent DFT (TD-DFT) computations to understand the spectroscopic difference between 2 and 5 (Figure 2). For



Figure 2. Energy-level diagram of **2** and **5** via TD-DFT computation. To avoid the convergence difficulties, the energy levels in the diagram are obtained via DFT optimization in the gas phase. The electronic transition energy, oscillation strength, and oscillation contribution are obtained from TD-DFT computation in chloroform.

the simulated UV-vis spectra of both compounds (Figures S6 and S7), the electronic transitions from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) are predominant (94.4% for 5 and 96.2% for 2), as evidenced by the strong oscillator strength (f = 0.80 for 5 and 0.72 for 2; Figure 2). The electron densities from HOMO to LUMO are distributed over the diacetylene BODIPY unit (Figure 2). Hence, it is assigned to the transition from π to π^* orbitals, which exemplify the intense absorbance of band I for both compounds 2 and 5 (Figure 1a).

For 5, the HOMO and LUMO energy levels are calculated to be -5.561 and -2.753 eV, respectively (Figure 2). In comparison, σ -platination destabilizes both the HOMO and LUMO energy levels (for 2, -5.082 eV for the HOMO energy level and -2.517 eV for the LUMO energy level; Figure 2). Evidently, the HOMO orbital is perturbed to a larger extent than the LUMO one. The result is primarily ascribed to the energy matching between the 5d orbital of platinum(II) and the HOMO of the diacetylene BODIPY unit.¹⁵ As a result, the HOMO–LUMO energy gap decreases from 5 to 2. The calculation is consistent with the experimental data, in which band I of 2 displays 75 nm more bathochromic shift than 5 (Figure 1a).

According to TD-DFT computation, bands II of both compounds originate from the electronic transition between low-lying HOMO-n and LUMO. For 5, it mainly comprises HOMO-6 to LUMO, as well as HOMO-4 to LUMO (compositions for the former and latter transitions are 86.6% and 88.0%, respectively; Figure 2). In terms of 2, it is assigned

to the HOMO-2-to-LUMO transition (the composition is 92.9%; Figure 2).

Visible-Light Photosensitization Capability of σ -Platinated BODIPY 2. The dual-emission character of 2 suggests that it can be excited and intersystem crossed to the triplet excited state. Successive energy transfer can take place between 2 and the surrounding molecular oxygen (Figure 3a).



Figure 3. (a) Schematic representation for the photosensitization of 2 to generate ${}^{1}O_{2}$ in situ. Time-dependent UV-vis spectra of (b) DMA (c = 0.20 mM for DMA and 0.004 mM for 2 in CHCl₃) under 525 nm irradiation (12.3 mW cm⁻²) and (d) 6 (c = 0.20 mM for 6 and 0.004 mM for 2 in CHCl₃) upon 590 nm irradiation (6.63 mW cm⁻²). (c) Linear fitting of the photooxygenation of DMA (c = 0.20 mM for DMA and 0.004 mM for 2 or 5 in CHCl₃): (▲ and ■) 525 and 590 nm irradiation with the presence of 2; (▼ and ●) 525 and 590 nm irradiation with the presence of 5. (e) Linear fitting of the photooxygenation of for the photooxygenation (6.63 mW cm⁻²): $c = (\blacksquare) 0.004$, (●) 0.008, (▲) 0.012, and (▼) 0.016 mM for 2.

In this regard, the photosensitization capability of **2** is examined by employing 9,10-dimethylanthracene (DMA) as the ${}^{1}O_{2}$ scavenger. 16 Briefly, DMA (c = 0.20 mM) and 2 mol % **2** are mixed together in CHCl₃. Upon green-light irradiation [light-emitting-diode (LED) lamp, 12 W, $\lambda = 525$ nm], the characteristic absorption bands of DMA ($\lambda_{max} = 360, 380, and 401$ nm) decline and completely disappear within 210 s (Figure 3b), suggesting the consumption of DMA. The time dependent absorbance curve conforms to the pseudo-first-order kinetics, providing a ${}^{1}O_{2}$ generation rate of 0.025 s⁻¹ for **2** (Figure 3c). Notably, the value is 2.8-fold higher than that of **5** under the same conditions (k = 0.0091 s⁻¹; Figures 3c and S8a), despite the fact that the molar absorption coefficient of **2** is significantly lower than that of **5** (at 525 nm, $\varepsilon = 6.00 \times 10^{3}$ dm³ mol⁻¹ cm⁻¹ for **2** vs 2.83 × 10⁴ dm³ mol⁻¹ cm⁻¹ for **5**).

Additionally, the photosensitization experiment is also performed via low-energy amber-light irradiation (LED lamp, 12 W, $\lambda = 590$ nm). Because 2 features intense absorption at 590 nm ($\varepsilon = 3.18 \times 10^4$ dm³ mol⁻¹ cm⁻¹ nm in CHCl₃), the ¹O₂ generation rate shows a further increase (k = 0.034 s⁻¹; Figures 3c and S8c). In stark contrast, the epoxidation product of DMA can hardly be probed for 5 under the same circumstances (Figures 3c and S8b), denoting the absence of ¹O₂ during the photoirradiating process. Although the iodosubstituted BODIPY 4 displays excellent photosensitization capability at 525 nm, it is unable to generate ¹O₂ under 590 nm irradiation (Figure S9c). The phenomena are highly reasonable, considering that both 4 and 5 possess weak absorption at 590 nm ($\varepsilon = 2.00 \times 10^2$ dm³ mol⁻¹ cm⁻¹ for 4 and 1.60×10^3 dm³ mol⁻¹ cm⁻¹ for 5 in CHCl₃). Hence, σ platination represents an efficient protocol to enhance the photosensitization capability of BODIPY under low-energy irradiation conditions.

On this basis, light irradiation is further performed for the mixture of 6 (0.10 mM) and 2 (2 mol %) (Figure 3d). Compound 6 possesses a 9,10-platinated anthracene unit, which is structurally similar to that of 1. Accordingly, 6 is capable of undergoing photosensitized oxygenation and can serve as a model system to evaluate the photoresponsiveness of 1. As can be seen, absorbance of the anthracene unit on 6gradually declines upon 590 nm light irradiation. In the meantime, the aromatic ¹H NMR resonances (8.68 and 7.46 ppm) weaken, while a new set of upshifted resonance peaks emerge (7.80 and 7.30 ppm; Figure S10). The results suggest the photooxygenation of 6 to the 9,10-endoperoxide product. The conversion rate from 6 to $6-O_2$ is determined to be 0.021 s^{-1} with 2 mol % of the photosensitizer 2, which shows a further increase at the higher amount of 2 (k = 0.043, 0.056, and 0.079 s⁻¹ for 4, 6, and 8 mol % of 2, respectively; Figures 3e and S13). On the contrary, no photooxygenation reaction takes place for 6 in the absence of 2 (Figure S11).

Supramolecular Polymerization and Gelation Behaviors of 1 in the Presence of 2. As previously demonstrated, 1 is capable of forming one-dimensional supramolecular polymers in a dilute methylcyclohexane (MCH) solution.^{5c} In concentrated MCH, supramolecular gels are prone to formation because of the entanglement of one-dimensional polymers to form fibrous networks.^{5c} Because 2 is totally not soluble in pure MCH, a small amount of chloroform is required to solubilize the photosensitizer. The polar chlorinated solvent is capable of weakening intermolecular hydrogen bonds in supramolecular polymers derived from 1. Hence, prior to a study of the photoresponsiveness of 1/2, the supramolecular polymerization and gelation capability of 1 should be reexamined with the presence of photosensitizer 2.

As widely documented, circular dichroism (CD) spectroscopy represents a powerful technique to probe the formation of supramolecular polymers.¹⁸ The supramolecular chirality signals are only present for long-range-ordered polymeric assemblies and absent for monomeric and small-sized oligomeric structures. To induce helical bias at the supramolecular level, optically active (S)-3,7-dimethyloctyl groups are introduced to the peripheral side chains of 1 (Scheme 1). For the mixture of 1 and 2 ($c = 1 \times 10^{-4}$ M for 1 and 2 × 10⁻⁶ M for 2), the Cotton effect is absent in pure chloroform (Figure 4a), suggesting the dominance of a molecularly dissolved state. In sharp contrast, the bisignate Cotton effect is present for 1/2 in MCH/CHCl₃ (97/3, v/v). The negative maximum is located at 487 nm, while the positive maxima are at 473 and 450 nm, respectively (at 283 K, $\Delta \varepsilon = -52.5$ L $mol^{-1} cm^{-1}$ and g = -0.0023 for 487 nm; Figure 4a). With reference to the UV-vis spectrum (Figure 4b), the CD signals originate from the ¹L_a transition band of the anthracene unit



Figure 4. (a) CD and (b) UV-vis spectra of 1/2 ($c = 1 \times 10^{-4}$ M for 1 and 2×10^{-6} M for 2 at 283 K) in (black line) CHCl₃ and (blue line) MCH/CHCl₃ (97/3, v/v). (c) Nonlinear fitting of the melting curves: (red line) 1 ($c = 1 \times 10^{-4}$ M) in pure MCH; (blue line) 1/2 ($c = 1 \times 10^{-4}$ M for 1 and 2×10^{-6} M for 2) in MCH/CHCl₃ (97/3, v/v). (d) Supramolecular gels of 1/2 (c = 12.8 mM for 1) and 1 (c = 13.7 mM for 1) in MCH/CHCl₃ (90/10, v/v).

on 1. The supramolecular chirality transfers from the alkyl periphery to the inner anthracene unit, supporting the formation of long-range-ordered supramolecular polymers in apolar MCH/CHCl₃ (97/3, v/v).

On this basis, we sought to understand the supramolecular polymerization thermodynamics by performing temperaturedependent CD measurements in MCH/CHCl₃ (97/3, v/v; c = 1×10^{-4} M for 1 and 2×10^{-6} M for 2). When the CD intensity at 486 nm versus temperature is monitored, a nonsigmoidal curve is obtained (Figures 4c and \$14). The result unambiguously suggests the involvement of a cooperative nucleation-elongation supramolecular polymerization mechanism.⁶ The quantitative thermodynamic parameters for the 1/2 supramolecular polymerization process can be further acquired by fitting the cooling curve by the Meijer-Schenning-van der Schoot mathematical model (see the Experimental Section).^{6d} Specifically, the enthalpy release (h_e) is determined to be -85.5 kJ mol⁻¹ for 1/2 in MCH/CHCl₃ (97/3, v/v; Figure 4c). The h_e value is relatively lower than that of 1 in pure MCH ($h_e = -95.5 \text{ kJ mol}^{-1}$; Figure 4c). Moreover, the critical elongation temperature (T_e) of 1/2 is determined to be 297.2 K, which is 15.8 K lower than that of 1 in MCH ($T_e = 313.0$ K). Overall, it can be concluded that onedimensional supramolecular polymers still form for 1/2 in $MCH/CHCl_3$ (97/3, v/v), although their stability is influenced by the small amount of chlorinated solvent. The nanofibers obtained from 1/2 can be directly confirmed by the transmission electron microscopy (TEM) measurements (Figure S15). Additionally, 1/2 is prone to forming supramolecular gels in concentrated MCH/CHCl₃ (90/10, v/v; critical gelation concentration = 12.1 mM). The dark-green color of 1/2 (Figure 4d) originates from the intense visiblelight absorption of the σ -platinated BODIPY photosensitizer 2.

Regulating the Photoresponsiveness of Supramolecular Polymers. Finally, we turned to regulating the photoresponsiveness of supramolecular polymers derived from 1 via the σ -platinated BODIPY photosensitizer 2. Upon amber-light (590 nm, 12 W) irradiation, the CD signals of 1/2 ($c = 1 \times 10^{-4}$ M for 1 and 2×10^{-6} M for 2) progressively decline and vanish within 40 min (Figure 5a). The disappearance of



Figure 5. (a) CD and (b) UV-vis spectral changes of 1/2 (c = 0.1 mM for 1 and 0.002 mM for 2 in MCH/CHCl₃ (97/3, v/v) upon 590 nm irradiation. (c) CD spectral changes of the mixture of 1-O₂ and 2 upon heating at 318 K. (d) Photoresponsiveness of supramolecular gels from 1/2 and 1.

supramolecular chirality reveals the disassembly of supramolecular polymeric structures. Meanwhile, the visible-light absorbance of 1 dramatically declines, accompanied by the presence of an isosbestic point at 357 nm (Figure 5b). The phenomenon suggests the conversion of 1 to its epoxidized structure (1-O₂). Remarkably, no spectroscopic changes take place for 1 in the absence of photosensitizer 2 (Figure S16). The results unambiguously support the crucial role of a σ platinated photosensitizer for the disassembly of supramolecular polymers under mild irradiation conditions.

On this basis, supramolecular repolymerization is investigated for the resulting mixture of $1-O_2$ and 2. As previously reported, the endoperoxide-to-anthracene conversion from 1-O₂ to 1 occurs spontaneously at room temperature and accelerates at elevated temperature.^{5c} As shown in Figure 5c, the CD signal is restored in MCH/CHCl₃ (97/3, v/v) upon heating of the sample at 318 K for 12 min. The re-formation of supramolecular chirality is attributed to the quantitative endoperoxide-to-anthracene transition of 1-O₂. The reversible photooxygenation process of 1/2 can be macroscopically visualized by "gel-sol" transition experiments (Figure 5d). Briefly, when 1/2 [c = 12.8 mM for 1 and 0.67 mM for 2 in $MCH/CHCl_3$ (90/10, v/v)] is irradiated for 60 min (590 nm), the supramolecular gel collapses to a dark-green fluid (Figure 5d), which converts back to a supramolecular gel upon standing at room temperature. In stark contrast, no "gel-to-sol" conversion takes place for 1 in the absence of photosensitizer 2 under the same amber-light irradiation conditions (Figure 5d).

3. CONCLUSION

In summary, σ -platinated BODIPY **2** has been designed as an efficient photosensitizer to regulate the photoresponsiveness of anthracene-based supramolecular polymers. For photosensitizer **2** itself, the metalation effect enhances π -electron delocalization of the BODIPY unit while promoting ISC

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from singlet to triplet excited states. As a result, 2 displays excellent ${}^{1}O_{2}$ production capability under green- and amberlight irradiation conditions. For the 1/2 mixed system, the in situ generated ${}^{1}O_{2}$ further reacts with 1 to form the endoperoxide product $1-O_{2}$, avoiding the harsh conditions (blue visible light or long-wave UV light) required for the conventional photooxygenation process. Accordingly, supramolecular polymers and gels break up upon low-energy visible-light excitation, which can be restored at room and elevated temperatures because of the reversible endoperoxide-to-anthracene deoxygenation process. Therefore, the current study opens up an effective approach to modulate the photoresponsiveness of supramolecular polymeric systems under mild conditions.

4. EXPERIMENTAL SECTION

Materials and Methods. All chemical reagents and solvents utilized in the preparation or testing procedure are commercially available and were received without further purification or isolation. BODIPY-based compounds 3-5 and trans-diiodobis-(triethylphosphine)platinum(II) were synthesized according to the previously reported literature.¹⁹ ¹H, ¹³C, and ³¹P NMR measurements were recorded on a Varian Unity INOVA-300 spectrometer with tetramethylsilane as the internal standard. A Bruker Autoflex Speed spectrometer was exploited with trans-2-[3-(4-tert-butylphenyl)-2methyl-2-propenylidene]malononitrile as the basic matrix. A Shimadzu UV-1800 spectrometer and a FluoroMax-4 spectrofluorometer were utilized to record the spectra of UV-vis absorption and fluorescent emission. For quantum yield measurements, rhodamine B ($\Phi_{\rm F}$ = 65% in ethanol) was employed as the standard reference.²⁰ The emission lifetime measurements were acquired with a 1 MHz LED laser with an excitation wavelength at 455 nm (NanoLED-455) and analyzed with DataStation v6.6 (Horiba Scientific). Supramolecular chirality signals for supramolecular assemblies were recorded on a Jasco J-1500-type CD spectrometer. During temperature-variable CD measurements, a PFD-425S/15 Peltier-type temperature controller was employed to precisely control the testing temperature of the cuvette. The cooling rate for cooling curve measurements is set as 1.0 K min⁻¹. For light irradiation experiments, 590 and 525 nm LED lamps (12 W) were exploited as light sources, by keeping the distance between the LED and cuvette at 10 cm. TEM images of 1 and 1/2were performed on a Tecnai G2 Spirit BioTWIN electron microscope.

DFT and TD-DFT Computation. DFT computations were performed by the *Gaussian 09*, D.01 version, software package.²¹ During optimization, nonmetallic atoms were described by the B3LYP/6-31G(d) computational level, while all platinum(II) atoms were described by the Lanl2dz effective core potential. The optimized geometries of 2 and 5 were utilized directly to compute feasible electronic transitions in CHCl₃ via TD-DFT.²²

Determination of the Assembling Thermodynamics of Supramolecular Polymers. To gain deeper insight into the supramolecular polymerization behaviors of 1 and 1/2 in different solvents, temperature-variable CD spectral measurements were performed. The resulting nonsigmoidal curves for the supramolecular polymerization process are divided into elongation and nucleation regimes, which are fitted by the Meijer–Schenning–van der Schoot mathematical model.^{6d}

For the elongation regime, the fraction of aggregated molecules (φ_n) can be calculated by eq 1.

$$\varphi_{\rm n} = \varphi_{\rm SAT} \{ 1 - \exp[(-h_{\rm e})(T - T_{\rm e})/RT_{\rm e}^2] \}$$
(1)

In eq 1, φ_{SAT} is introduced to prevent the relationship $\varphi_n/\varphi_{\text{SAT}}$ from surpassing the value of 1. h_e denotes the enthalpy release during the elongated supramolecular polymerization regime. T_e denotes the critical elongation temperature, whereas T denotes the absolute temperature during the supramolecular polymerization process.

Synthesis of σ -Platinated BODIPY 2. trans-Diiodobis-(triethylphosphine)platinum(II) (380 mg, 0.55 mmol) and CuI (5 mg, 0.025 mmol) were added to a 50 mL Schlenk flask and cooled to -78 °C. The deprotected form of 5 (91 mg, 0.25 mmol) in THF (10 mL) was injected into the flask, followed by the successive addition of $(i-Pr)_2$ NH (4 mL). The resulting solution was stirred at -78 °C for 1 h and then stirred at room temperature overnight. The dark-green product was purified by a silica gel column (eluent: petroleum ether/ ethyl acetate = 9/1, v/v) to afford 2 as a dark-green powder (130 mg, yield 35%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.48-7.47 (3H, C₆H₅), 7.29-7.28 (2H, C₆H₅), 2.62 (s, 6H, CH₃), 2.18-2.11 (m, 24H, PCH₂CH₃), 1.38 (s, 6H, CH₃), 1.15-1.07 (m, 36H, PCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 156.9, 140.3, 139.9, 135.6, 130.9, 129.1, 128.9, 128.3, 121.1, 95.9, 95.8, 95.6, 91.5, 29.8, 16.9, 16.7, 16.5, 13.8, 13.3, 8.5, 8.4, 8.3. ³¹P NMR (162 MHz, CDCl₃): δ 9.00 (s, ${}^{1}J_{Pt-P} = 2345.8$ Hz). MALDI-TOF ([M]⁺): m/z1486.7575.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02073.

Synthesis, characterization, spectroscopic data, and other materials (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 21922110, 21674106, and 21871245), the Fundamental Research Funds for the Central Universities (Grant WK3450000004), the CAS Youth Innovation Promotion Association (Grant 2015365), and State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University (Grant 20182009).

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